

During the late 1950's and early 1960's, Charles D. Keeling supervised the measurement of pCO<sub>2</sub> in surface ocean waters and in the atmosphere just above on a number of seagoing expeditions mounted by Scripps Institution of Oceanography. These expeditions ("cruises"), comprising long transects in the major oceans, were chosen to map the global features of surface ocean pCO<sub>2</sub>. Data from most of these cruises are presented here for the first time in detail (in the form of hourly averages). The data had been processed soon after the cruises and presented in several research articles as averages, over geographical areas, of the difference in CO<sub>2</sub> concentration between ocean and atmosphere (see References). This site contains data from the DOWNWIND cruise in 1957, the MONSOON cruise in 1961, and the long LUSIAD cruise in 1962 and 1963.

The data sets are as prepared by Lee S. Waterman [Waterman et al, 1996], with the addition of a column containing  $\Delta X$ , the difference between the measured mixing ratio (or mole fraction "X") of CO<sub>2</sub> in the gas streams, one flowing through a sea water equilibrator and the other directly from the atmospheric intake. Both streams were dried air, having passed through a cold trap. Concerns about infrared analyzer detector drift (due to leakage of filling gas) and about calibration of the analyzer have not been resolved. Substantial uncertainty may never be eliminated for the individually measured mixing ratios  $X_{\text{air}}$  and  $X_{\text{eq}}$ . The difference between the mixing ratios of CO<sub>2</sub> in the surface seawater and in the air above ( $\Delta X = X_{\text{eq}} - X_{\text{air}}$ ), however, is likely to be reliable, as it will be much less dependent upon the uncertainties of calibration. Drift issues (for example due to detector leakage) are not relevant, since the two mixing ratios are measured nearly simultaneously.

Leakage of the filler gas in the acoustic detectors of non-dispersive infrared analyzers (NDIRs) affects the NDIR sensitivity, which was tracked by periodic calibrations during the period of analyses. It also causes changes in the "carrier gas effect," due to absorptive energy line-broadening [Griffith et al, 1982]. The carrier gas effect was quantified by the Scripps CO<sub>2</sub> Program for its measurement system in 1974 [Guenther and Keeling, 1981], and found to be equal to about 4 ppm in mole fraction of CO<sub>2</sub> (at approximately the mole fraction of the atmosphere) for the Applied Physics Corporation (APC) NDIR in use in the SIO laboratory at that time. On these cruises CO<sub>2</sub> - in - N<sub>2</sub> reference gases were used to define the X of CO<sub>2</sub> in the streams of air; thus a correction for the carrier gas effect must be made when calculating the X in air from the NDIR voltages. The correction is very dependent upon the gas composition of the detector fill gas (especially the CO<sub>2</sub> content: approximately 1.3% (in Argon) in the APC detectors) and upon the optical characteristics of the NDIR. The magnitude of the carrier gas effect varies among NDIRs from different manufacturers (for example, the German analyzers URAS, UNOR, and Siemens). Measurable variations were also found between NDIRs of the same make [Griffith et al, 1982].

Since the carrier gas effect is the same for the atmospheric and the equilibrated air measurements made close together in time, the difference  $\Delta X$  of CO<sub>2</sub> between the equilibrated surface seawater and atmospheric air streams is nearly independent of changes or drift in the carrier gas effect. The X's listed for the measured streams of gas ( $X_{\text{eq}}$  and  $X_{\text{air}}$ ) in the data sets are calculated from the NDIR voltage outputs using the cubic calibration equation for CO<sub>2</sub> - in - air from the 1983 and 1985 calibrations of the APC NDIR [Keeling et al, 1986]. Therefore the X's in the data sets have been corrected for carrier gas effect, but assuming that the effect was the same on the seagoing APC analyzers during the 1957-1963 cruises as it was in 1983-1985 on the laboratory APC analyzer. The NDIR response was also assumed to be the same as defined by the cubic equations in 1983-1985. We know that the carrier gas effect for the SIO laboratory instrument was stable from 1974 to 1985, but prior to 1973 the detectors were prone to leakage. In summary, the data sets present individual mixing ratios (X) for the two gas streams assuming that the APC NDIRs at sea from 1957 to 1963 had a cubic relation of the mole fraction of CO<sub>2</sub> to the voltage output of the NDIR and a carrier gas effect identical to that of the SIO laboratory instrument in 1983 and 1985.

The atmospheric air stream on the LUSIAD cruise displayed a diurnal cycle in measured CO<sub>2</sub> mixing ratio [Waterman et al, 1996, p. 20-21], likely caused by degassing of the plastic airline when exposed to sunlight. Only nighttime air data was considered free of this effect and thus acceptable. There is an additional column containing a flag in the LUSIAD data sets, specifically a "1" for the accepted nighttime data. The listed  $\Delta X$  values for non-flagged data are considered to be unreliable.